



AFRL-OSR-VA-TR-2013-0282

**ADVANCING THEORETICAL METHODS TO INVESTIGATE
REACTIONS ON ORGANIC SURFACES IN VARIOUS ENERGY
REGIMES**

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08-05-2013

Final Report

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Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/RTB1
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 08-05-2013		2. REPORT TYPE FINAL		3. DATES COVERED (From - To) 01-05-2009 30/11/2012	
4. TITLE AND SUBTITLE ADVANCING THEORETICAL METHODS TO INVESTIGATE REACTIONS ON ORGANIC SURFACES IN VARIOUS ENERGY REGIMES				5a. CONTRACT NUMBER FA9550-09-1-0184	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) DIEGO TROYA				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) DEPARTMENT OF CHEMISTRY VIRGINIA TECH 107 DAVIDSON HALL, BLACKSBURG VA 24061-0212				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AIR FORCE OFFICE OF SCIENTIFIC RESEARCH 875 NORTH RANDOLPH STREET ARLINGTON, VA 22203-1768				10. SPONSOR/MONITOR'S ACRONYM(S) ONRRO	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT DISTRIBUTION A: Distribution approved for public release.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This final report details the progress made in the development of new computational techniques to study the dynamics of chemical processes at the gas-surface interface with unprecedented levels of accuracy. Two main goals have been accomplished. First, the dynamics of inelastic collisions of gases from organic surfaces that exhibit strong hydrogen-bonding interactions have been deciphered by combining high-accuracy potentials derived from ab initio calculations with trajectory calculations. Second, the dynamics of collisions between gaseous radicals and organic surface have been revealed by developing a hybrid quantum mechanics/molecular mechanics approach in which very efficient and accurate methods are used for the quantum mechanics part. Comparison with available experiments served to guide and calibrate the accuracy of the developed computational techniques. A majority of the work performed under this contract has been disseminated to the community via various publications in peer-reviewed journals, and a few more manuscripts are under preparation.					
15. SUBJECT TERMS Computational chemistry. Theoretical chemistry. Gas/surface energy exchange. Reaction dynamics on surfaces.					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON DIEGO TROYA
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code) 540-231-1381

Final Performance Report

A complete characterization of the dynamics of gas-surface phenomena requires intimate knowledge of the atomic motions as a gas approaches, collides, and reacts or transfers energy with an organic surface. The timescale for such process is very fast (in the subpicosecond regime), and therefore revealing such motions with an experimental approach is exceedingly difficult. Instead, experimental approaches commonly aim molecular beams with well-characterized translational energies to a surface and obtain information about the gas-surface interaction by interrogating the recoiling gas-phase species after collision, by probing the surface, or both. It is in this context that computational approaches to reaction dynamics emerge as an extremely useful complement to the experiment. In effect, the ability to monitor the coordinates and velocities of each atom in a gas-surface collision via molecular dynamics enables a complete description of the dynamics of the interaction in a way that is not readily available from experiments. However, utilization of molecular dynamics techniques to investigate gas-surface processes is tremendously challenging mainly because there is not a clear strategy to derive a potential energy surface with enough accuracy to be able to capture experimental results that is not computationally prohibitive.

The work developed in this granting period was aimed at advancing theoretical techniques to overcome the technical barriers posed by the need to fully understand the dynamics of gas-surface reactions. The major advances accomplished in this work consisted of developing strategies to obtain accurate and efficient potential energy surfaces that can be conveniently used in trajectory calculations of gas-surface collisions. Progress was made in the development of potential energy surfaces for two distinct types of collisions: non-reactive (inelastic) and reactive. Details of such progress are provided independently for each of the types of collision events below. The organic surfaces of choice were mostly self-assembled monolayers, but toward the end of the granting period calculations on liquids were also accomplished.

In the following, the technical aspects of the potential-energy-surface development work are detailed first. Subsequently, results of trajectory calculations that utilized those potential energy surfaces are reported.

Potential energy surfaces

1) Non-reactive collisions.

Many recent experiments have characterized the dynamics of energy transfer in collisions of inert gases with organic surfaces using either molecular beams with time-of-flight detection of the scattered gas species to obtain translational-energy information, or using spectroscopic detection to reveal internal-state distributions. To further understand the aspects of the gas-surface collisions not available in the experiment, trajectory calculations were carried out under this grant. The calculations required derivation of accurate potential energy surfaces, which were developed according to the following approach.

The entire potential energy surface capturing the interactions in a non-reactive gas-surface system can be divided into three terms: i) the potential describing the interactions between atoms of the surface, ii) the potential of the interactions between the atoms of the gas species, iii) the potential for the gas-surface interactions. Because the energy with which the gas species impacts the surface is relatively low, and is absorbed by various groups on the surface, dramatic deviations of surface chains from their equilibrium structures during collisions are uncommon. Therefore, published harmonic force fields such as OPLS generally provide a good representation of the surface potential and are commonly used without modification. The same rationale applies to the gas potential, which for diatomic molecules is usually represented by a Morse potential that reproduces experimental rovibrational constants.

In contrast, extensive simulations carried out under prior granting periods showed that intermolecular gas-surface potentials from published force fields or gas-phase experiments lack the accuracy required for quantitative agreement with experiment. Therefore, the gas-surface potential is generally derived for each system under consideration using *ab initio* calculations. For simplicity, this intermolecular potential is considered to be pair-wise, so that the total interaction of the gas with the surface is a sum of the individual interactions between two atoms of each species. The Buckingham potential, $V_{ij}(r_{ij}) = A_{ij} \exp(-B_{ij}r_{ij}) + C_{ij}/r_{ij}^{D_{ij}}$, where the *A-D* terms are adjustable parameters specific to each pair of atoms, *ij*, and r_{ij} is the distance between the two atoms, is adopted for each pair of atoms that fall within an interaction distance cutoff of about 10-12 Å. Note that the sign of the *C* coefficient is negative so that it represents attraction, and that if only dispersion interactions are present, the exponent D_{ij} is commonly fixed to 6. The values of the *A-D* parameters for each

pair of atoms are chosen from a fit of the sum of the pairwise Buckingham potentials for a gas-phase model of the gas-surface system to high-level *ab initio* calculations. Thus, for simulations of collisions of, say, Kr with hydrocarbon self-assembled monolayer (CH₃-SAM), *ab initio* calculations of various approaches of Kr to CH₄ are carried out, and the A-D Buckingham parameters for the Kr-C and Kr-H pairs are determined by a fit of the Buckingham function to the *ab initio* results.

For collisions involving rare gases or symmetric molecules like CO₂ the *ab initio* calculations of prior work considered only a handful of approaches of the gas to the organic. On the other hand, the lack of symmetry about their center of diatomic molecules like OH and HCl required *ab initio* calculations that explored the possibility that the molecule collides with each of its dissimilar ends first in this work. This complication increased the number of *ab initio* points and thus the computational expense of this step of the simulation work. Furthermore, while most of the inelastic-scattering studies have considered closed-shell gas-phase species, recent studies on OH and NO scattering from fluorinated SAM surfaces highlighted the interest in extending the understanding of gas-surface energy transfer to open-shell species. In the case of OH, the ²Π nature of the ground state implies that there are two surfaces participating in the scattering. Following work on gas-phase inelastic scattering, collisions of OH with a structureless closed-shell target within the same spin-orbit manifold should be modeled on the average potential of the two intervening surfaces. This procedure was adopted to investigate OH collisions with an F-SAM in this grant, where it was shown that the scattering on the ground-state surface provides different results than on the average surface. The incorporation of more than one potential energy surface in the *ab initio* calculations necessarily involves a greater computational overhead, which for the OH/F-SAM studies entailed the calculation of over 1,000 *ab initio*. Figure 1 shows these *ab initio* energies calculated in the development of an accurate potential energy surface for collisions of OH collisions with a fluorinated SAM surface together with pictorial representations of the approaches.

To compute the *ab initio* grid of points necessary for the derivation of the gas-surface potential, use of an electronic-structure method capable of capturing dispersion interactions was paramount. Coupled-cluster theory, with single, double, and perturbative triple excitations (CCSD(T)) was the common method of choice. Regarding the basis sets, calculations with the aug-cc-pVNZ (N=D,T,Q) series provided a convenient way to obtain complete basis set extrapolations. These type of calculations became costly in systems involving many

electrons (e.g. OH+CF₄, for OH+F-SAM simulations), and the focal-point approximation, which enabled accurate estimates of CCSD(T) energies from more inexpensive MP2 calculations, proved extremely useful. Using this approach, potential energy surfaces for collisions of both OH with and F-SAM and HCl with a hydroxyl-terminated SAM (OH-SAM) were derived. Results of the corresponding trajectory calculations are described below.

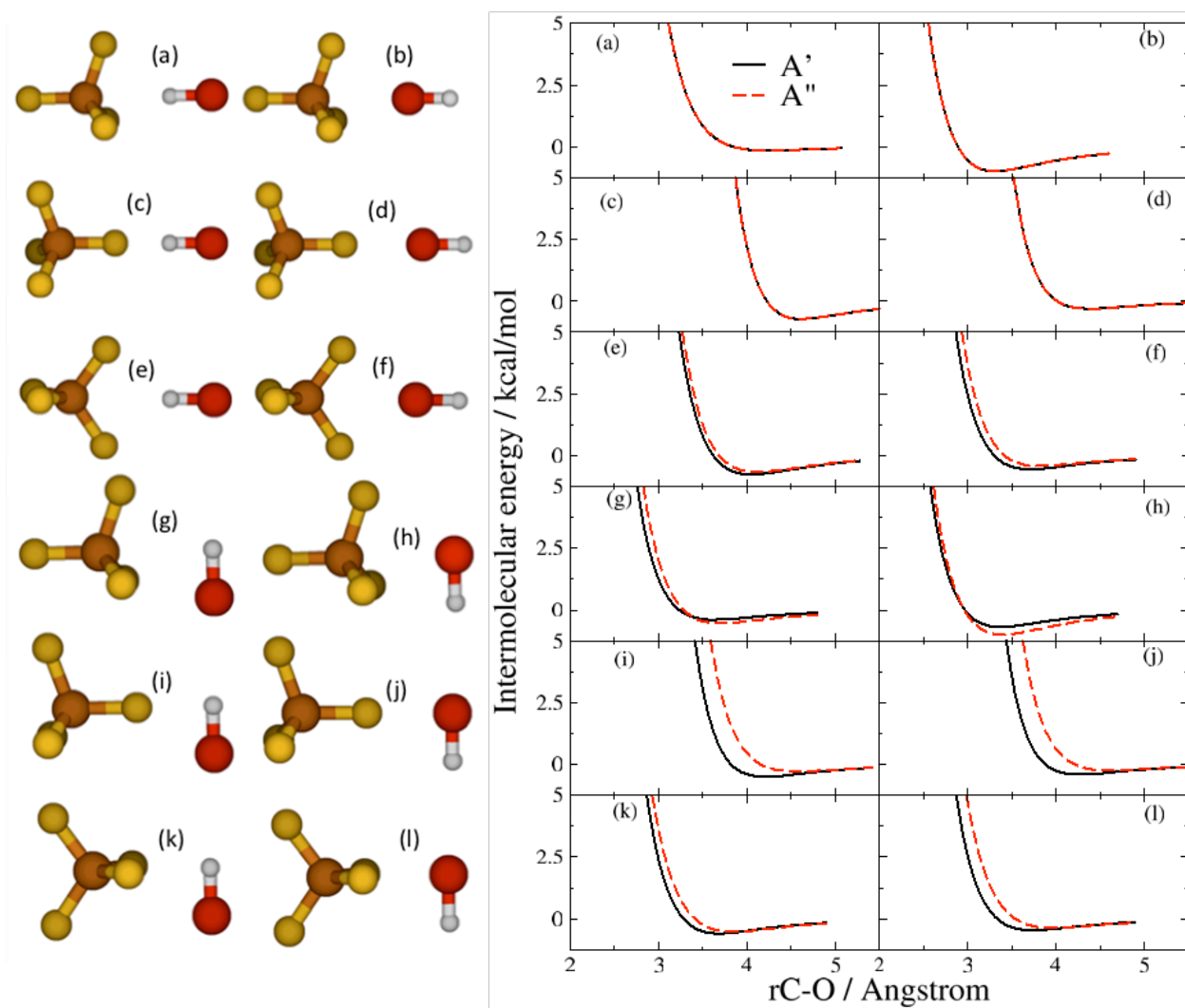


Figure 1. (Left) Approaches of OH to a fluorinated species considered in the development of a potential energy surface for OH collisions with F-SAMs. (Right) fp-CCSD(T)/aug-cc-pVQZ energies on both A' and A'' surfaces for each approach.

2) Reactive collisions.

Use of harmonic force fields for the inelastic-scattering simulations described in the prior section limits the applicability of the methods to systems in which there is no bond breakage/formation. Therefore, simulation of reactions between gases and surfaces required a new form of potential energy surface that allows bond dissociation. Drawing upon the state of the art in the field of gas-phase reaction-dynamics calculations, there are

two main strategies to obtain the forces acting on the nuclei during a trajectory simulation of a chemical reaction. First, fitted or interpolated potential-energy surfaces can be obtained from a representative set of *ab initio* points. A drawback of this approach is that current algorithms are restricted to systems with a few atoms, which makes it difficult to seek application in reactions involving organic surfaces. Second, an electronic-structure calculation of the energy gradient can be performed “on the fly” whenever needed to solve the equations of motion of the nuclei. This technique is commonly known as direct dynamics. A disadvantage of direct dynamics is that conventional trajectory studies of chemical reactions require millions to billions of energy gradients, and this constrains significantly the accuracy of the electronic-structure methods that can be used. On the other hand, direct dynamics is a general technique that can be applied to gas-surface reactions, and in fact, this is the strategy that has been more frequently used in the few simulations of reactions involving organic surfaces available until now.

An important aspect of using direct dynamics to evolve trajectories of gas-surface reactions is that the large number of atoms used in regular simulation cells makes most electronic-structure calculations prohibitive. Realizing that when a radical strikes an organic surface, potential bond breaking and formation likely occurs in the vicinity of the impact region, all of the studies have invoked a division of the gas-surface system into an active region, where bond rearrangement takes place, and an inactive region, which provides structural support. This separation conveniently allowed for implementation of quantum-mechanics/molecular-mechanics (QM/MM) algorithms in this grant, in which only the active section necessitates computationally intensive quantum-mechanical methods; the inactive region can be accurately treated with inexpensive harmonic force fields.

Despite use of QM/MM technology ameliorating the computational expense of the calculations, the active region was too large to use cutting-edge *ab initio* methods. For instance, in QM/MM calculations of reactions of radicals with SAMs, the active region comprises the striking gas-phase radical and the ethyl or butyl termini of a central alkanethiol chain and the six nearest-neighbor chains. This standard active region includes well over 100 valence electrons, which significantly limits the QM methods with which one can compute millions to billions of energy gradients to semiempirical theory. Since semiempirical methods rarely exhibit the accuracy necessary to reproduce experiment, the emerging strategy that was used in this grant to

improve their accuracy was to optimize the parameters contained in the solution of the electronic Schrödinger equation specifically for each gas-surface reaction under consideration. The promise showed in a prior granting period by specific-reaction-parameters (SRP) semiempirical Hamiltonians in the gas phase, where they were able to reproduce both high-level *ab initio* data in the reaction swath and experiment, warranted their use in gas-surface calculations as well. Using this approach, an SRP Hamiltonian was developed for F+alkane reactions, which enabled investigation of the dynamics of F+SAM reactions that produce HF. Experimental information on this reaction was provided by the Nesbitt group. Figure 2 shows the QM/MM scheme utilized in the trajectory calculations of F+SAM collisions, and the entrance channel of that potential energy surface. Results of such calculations are presented below

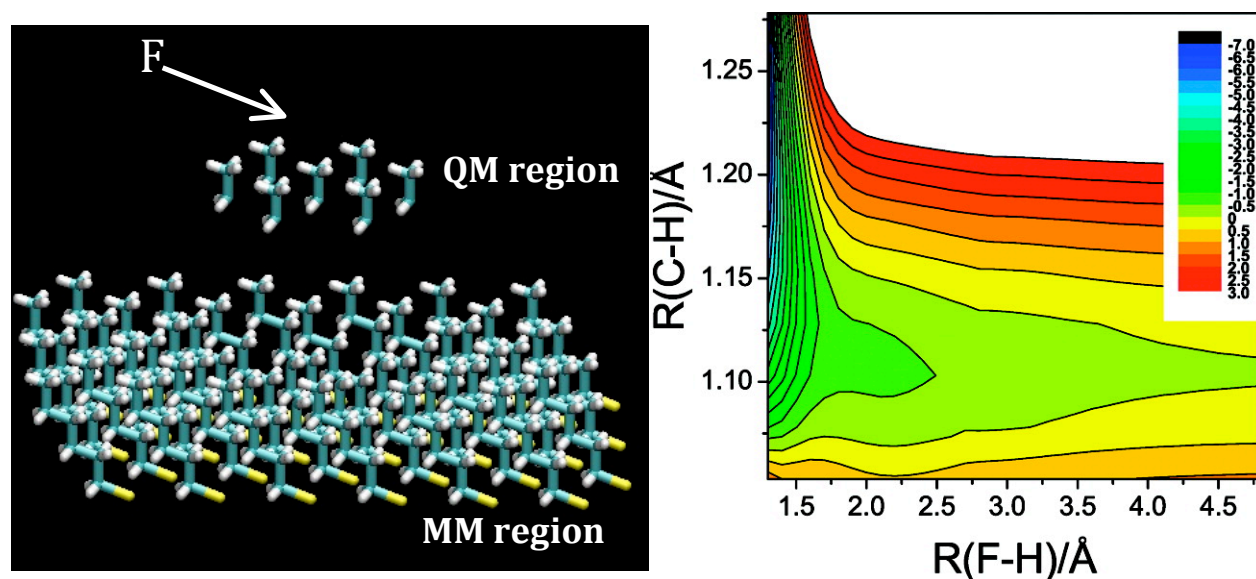


Figure 2. (Left) QM/MM partitioning of the potential energy surface in trajectory calculations of F+alkanethiol self-assembled monolayer collisions. (Right) Entrance channel of the potential energy produced by a specific-reaction-parameters semiempirical Hamiltonian for F+alkane reactions. Energy scale in kcal/mol.

Trajectory calculations

Employing the potential energy surfaces derived according to the strategies reported above, trajectory calculations of gas-surface collisions were conducted. Various systems were considered, including collisions of HCl with a hydroxyl-terminated SAM, OH with a fluorinated SAM, and fluorine with a hydrocarbon self-assembled monolayer.

1) HCl+OH-SAM inelastic collisions

Molecular-beam experiments in the Morris lab had provided details about the energy transfer in collisions of gaseous HCl with a hydroxyl-terminated self-assembled monolayer. Trajectory calculations were performed under the auspices of this grant to fully understand the experimental results and provide mechanistic information not directly available from the experiment. The calculations were especially challenging because the interactions of HCl with an OH-SAM are significantly stronger than the dispersion-type interactions investigated in all prior inelastic gas-surface work. Indeed, the potential presence of hydrogen bonding between the gas and the surface opened the door for a new realm of dynamical processes that entail long residence times of the gas on the surface. Figure 3 shows the HCl product energy distributions obtained from the trajectory calculations in comparison with experiment. Excellent agreement is found between calculations and measurements for the fit of the ab initio data that considered an explicit Coulomb term in the potential energy surface. The ensuing major conclusion of that work was that for relatively strong intermolecular interactions between gases and surfaces, standard non-bonding potential energy surfaces are not sufficiently accurate to capture experiment.

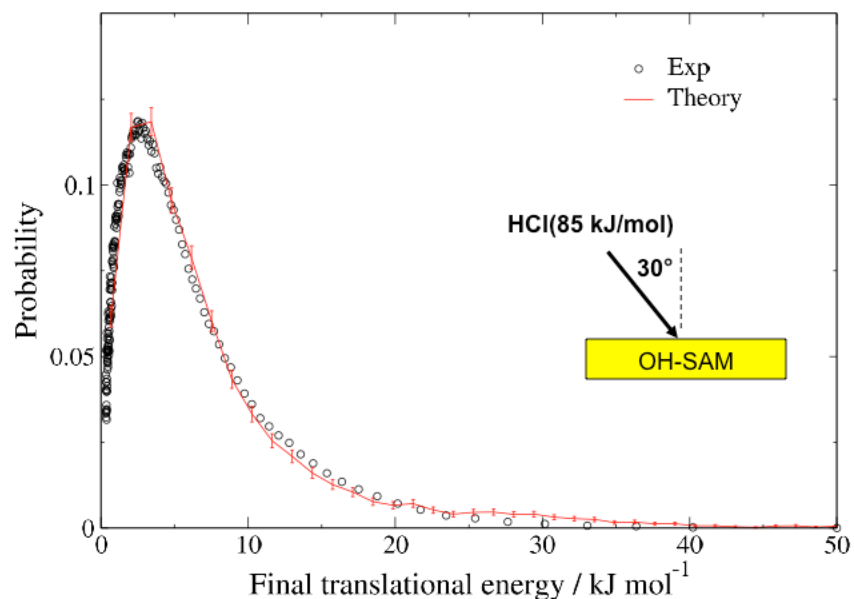


Figure 3. Calculated and measured product translational energy distributions in collisions of HCl with hydroxylated self-assembled monolayers.

The calculations also helped reveal the mechanism of the gas-surface interaction. At high collision energies (85 kJ/mol), there are three main types of collisions, direct (22%), short-lived, in which the HCl molecule resides on the surface for a few ps before desorbing (9%), and long-lived, in which strong hydrogen bonds between HCl and the surface inhibit HCl desorption beyond the nanosecond timescale (69%).

2) OH+F-SAM inelastic collisions

Recent experiments by McKendrick reported rovibrational state distributions of OH after collision with fluorinated surfaces. Much as with the rest of experimental probes of gas-surface scattering, the experiments only characterize how the energy of the gas and surface change during the course of the collision, but cannot provide a complete description of the mechanism. In this work, trajectory calculations of OH collisions with fluorinated surfaces were conducted to facilitate the mechanistic understanding of such processes. The potential energy surfaces are shown in Figure 1 above. A significant challenge in the calculations was the fact that in the experiment, photolysis is used to generate OH, which emerges with a distribution of rotational states prior to collision. Therefore, to make contact with experiment, trajectory calculations in which OH initially possesses given discrete rotational quantum numbers were required. After averaging the trajectory results over all contributing initial rotational states, the agreement provided by our calculations with the experiments of McKendrick is very good (Figure 4).

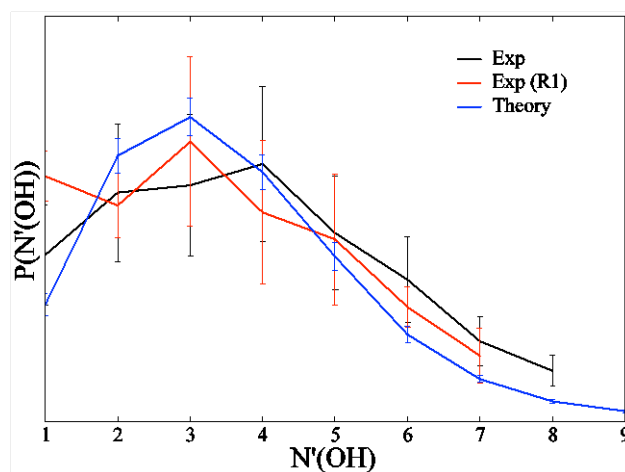


Figure 4. Comparison of experimental and calculated rotational OH distributions after collisions with a fluorinated self-assembled monolayer.

In addition to providing deeper understanding of experiments, the calculations also sought to understand how the physical state of the surface (liquid, or semicrystalline such as in a self-assembled monolayer) affects the energy transfer in gas collisions. Trajectories were therefore propagated to compare the dynamics of OH in collisions with a fluorinated self-assembled monolayer and a fluorinated liquid. The calculations revealed subtle differences between the two surfaces, which were attributed to the rougher aspect of the liquids. In general, the ordered nature of organic monolayers was found to make them more efficient energy absorbers than liquids, and this agrees with experimental findings by McKendrick.

3) F+SAM reactive collisions

Undoubtedly, the cornerstone accomplishment of this grant was the investigation of reactions of fluorine radicals with self-assembled monolayers. Experiments by Nesbitt triggered earlier computational studies, but they could not capture the experiments quantitatively due to inaccuracies in the potential. Using the methodology described above to generate accurate potential energy surfaces for reactive gas-surface collisions, a thorough investigation of the reaction dynamics was carried out using trajectories. Figure 5 shows a comparison of vibrational-state-specific HF rotational distributions emerging from F collisions with alkane surfaces.

As Figure 5 shows, the agreement between theory and experiment was found to be very good. As a matter of fact, such level of agreement was unprecedented for this type of systems. The agreement between theory and experiment also served to validate the computational techniques developed in this grant and afforded mechanistic studies that complemented previous experimental efforts. In this vein, an analysis of the microscopic mechanism of a gas-surface reactive collision is shown in Figure 5 (right panels). The top panel shows the coordinate of a fluorine radical in the surface-normal axis in a collision with a SAM surface that generates HF. From the figure, it seems that the collision is direct, i.e., fluorine simply approaches the surface, collides with it, and abstracts a hydrogen atom without spending much time on the surface. However, the lower panel presents a far richer perspective on the same collision by plotting the vibrational and rotational quantum numbers as a function of time. The vibration quantum number is established immediately after abstraction by F. On the other hand, the HF rotation is not established right away. Instead, during the desorption pathway, strong

interactions between the just-formed HF molecule and the surface alter the rotational energy of the molecule. This level of description of the microscopic reaction mechanism proved fundamental in the understanding of gas-surface collisions.

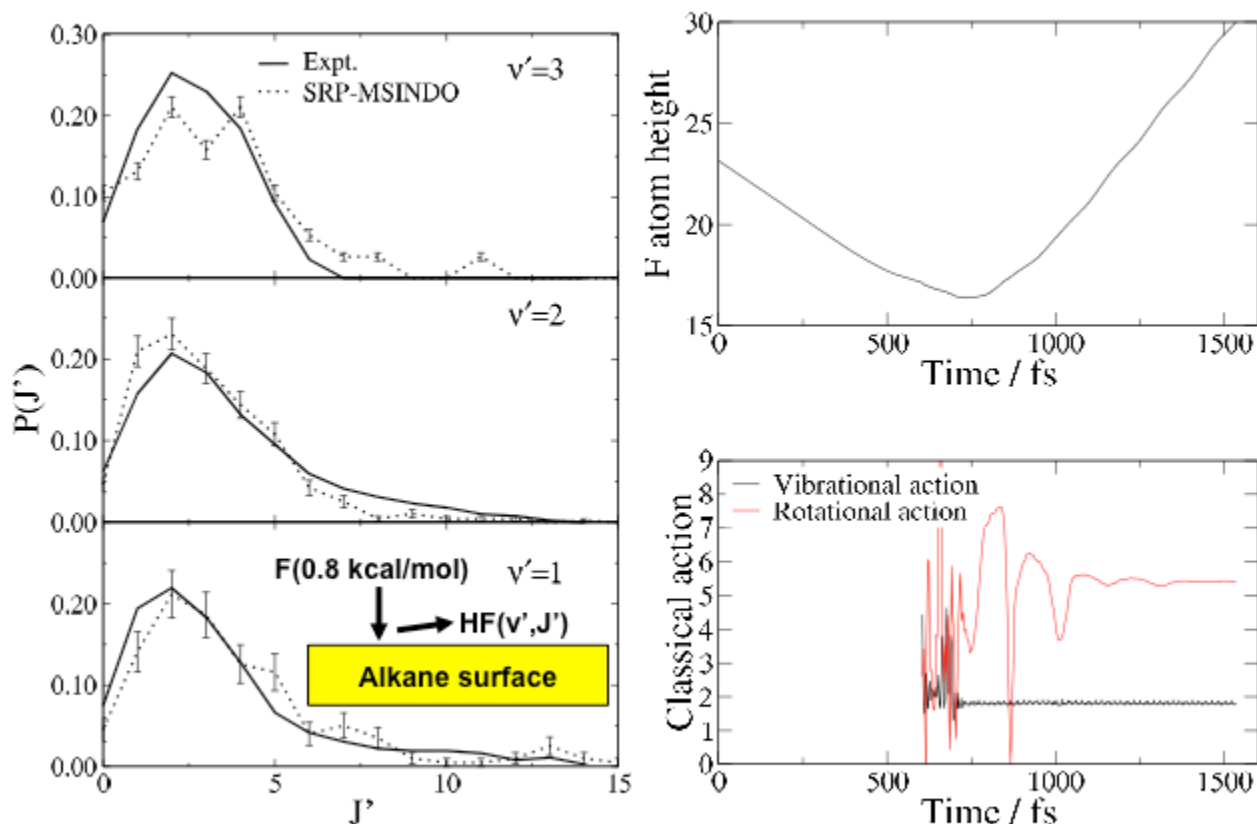


Figure 5. (Left) Rovibrational distributions of nascent HF in F collisions with organic surfaces. (Right) F atom height above the surface (top), and rovibrational action (bottom) in a sample F+SAM trajectory.

4) Additional efforts

In addition to the accomplishments described until now, additional target-of-opportunity work was published in peer-reviewed journals, including a study of the dynamics of hyperthermal oxygen atoms with hydrazine, a common propellant in spacecraft. Many of our efforts were summarized in an extensive review paper in “Progress in Surface Science” written in collaboration with experimental collaborators. See below.

Publications list

1.- Direct-dynamics study of the $F+CH_4$, C_2H_6 , C_3H_8 , and $i-C_4H_{10}$ reactions

J. P. Layfield, A. F. Sweeney, and D. Troya

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J. Phys. Chem. A 113, 4294 (2009)

2.- *Ab initio and dynamics study of the $O(3P)+NH_3$ and $O(3P)+N_2H_4$ reactions at hyperthermal collision energies*

D. Troya, M. Mosch, and K. A. O'Neill

J. Phys. Chem. A 113, 13863 (2009)

3.- *Theoretical study of the dynamics of F+alkanethiol self-assembled monolayer hydrogen-abstraction reactions*

J.P. Layfield and D. Troya

J. Chem. Phys. 132, 134307 (2010)

4.- *Theoretical study of the dynamics of collisions between HCl and ω -hydroxylated alkanethiol self-Assembled monolayers*

W. A. Alexander and D. Troya

J. Phys. Chem. C 115, 2273 (2011)

5.- *Dynamics of collisions of hydroxyl radicals with fluorinated self-assembled monolayers*

D. Troya

Theoretical Chemistry Accounts 131, 1072 (2012)

6.- *Interfacial energy exchange and reaction dynamics in collisions of gases on model organic surfaces*

J. W. Lu, B. S. Day, L. R. Fiegland, E. D. Davis, W. A. Alexander, D. Troya, and J. R. Morris

Progress in Surface Science 87, 221-252 (2012)

7.- *Trajectory study of collisions of OH with liquid and solid fluorinated surfaces*

D. Troya

In preparation

8.- *Theoretical studies of the $OH+C_2H_4$ and $OH+C_3H_6$ reactions*

J. Zhang, and D. Troya

In preparation